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SOLID LUBRICANTS FOR IMPROVED WEAR RESISTANCE.(U)
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SOLID LUBRICANTS FOR IMPROVED WEAR RESISTANCE

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Detailed studies including synthesis, characterization and evaluation of antimony thioantimonate, $SbSbS_4$, were carried out. As a solid lubricant additive in various greases, this material exhibited superior extreme pressure and antiwear properties as demonstrated by the Four-Ball weld points and load-wear indexes

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on both AISI-52100 and AISI-440C steels. Moreover, impressive abrasive wear resistance properties were imparted by low concentrations of $SbSbS_4$ in greases deliberately contaminated with hard abrasive particles. This additive appeared to be compatible with all the base greases investigated including a silicone grease in which very few additives show good response.

The lubricant properties of a number of cerium and zinc thio- and oxythiomolybdates were also investigated. The cerium complexes, as additives in a lithium grease, showed excellent antiwear properties on both chrome tool and stainless steel. However, their non-stoichiometric composition and tendency to form hydrates caused complications during synthesis and evaluation of properties. The zinc complexes were found to be even more promising as antiwear additives, especially for high temperature use on stainless steel.

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SOLID LUBRICANTS FOR IMPROVED WEAR RESISTANCE

A. OBJECTIVE

This program was for development of superior extreme pressure, antiwear, thermally stable lubricants and lubricant additives for use in both conventional and corrosion resistant metal surfaces. It was the objective of this task to extend the useful life of Navy lubricated bearings, seals, splines, aircraft arresting cables, and sliding metallic surfaces. Lubricants for corrosion resistant metals are particularly desirable because the use of these metals in corrosive environments is often precluded by the lack of lubricants suitable under these conditions.

B. INTRODUCTION

The approach investigated in this program was a follow-up to an earlier study carried out at Pennwalt's laboratories with partial support by the U. S. Navy and where a number of complex metal chalcogenides had been examined[1-4] for their performance as extreme pressure and antiwear additives in greases, solid film lubricants, and fluids. As extreme pressure and antiwear additives, these complex chalcogenides had been found superior to simple sulfides, including MoS_2. One composition, arsenic thioantimonate was a particularly outstanding solid lubricant and, therefore, became the subject of much characterization and evaluation.[2] When the safety of all inorganic arsenic compounds came under question, further development of arsenic thioantimonate was terminated. However, under that program other promising leads had been uncovered and which were then selected for additional studies in a subsequent effort whose results are summarized in this report. Of particular interest was antimony thioantimonate ($SbSbS_4$) which received special attention in this study. Other promising materials described

in this report include cerium and zinc oxythiomolybdates. While $SbSbS_4$ was found to be an outstanding extreme pressure lubricant additive with unique antiabrasive properties, the oxythiomolybdates were noteworthy for their antiwear characteristics and high thermal stability.

C. ANTIMONY THIOANTIMONATE - $SbSbS_4$

1. General

Laboratory synthesis and performance data on $SbSbS_4$ are described in detail in the attached copies of publications (Appendix I and II). The preparative method reported in Appendix I represents an improved reaction route with greater simplicity, reproducibility, product priority, and higher yield compared with the original method.[3] Commercial production of $SbSbS_4$ should be possible without a major process development effort. A cost estimate for the production of several million pounds of $SbSbS_4$ has shown that this product can be made available at a price comparable to, and possible lower than, that of molybdenum disulfide, MoS_2.

2. Field Tests

Field tests with greases containing $SbSbS_4$ are being carried out by the Marine Corps at Camp Lejeune, NC, on high mobility vehicles. Another series of field tests is expected to start shortly at a Marine Corps base in California.

Test results to date from Camp Lejeune (after about one year of use in heavy duty vehicles) indicate that grease with $SbSbS_4$ as an additive is greatly superior to the standard GAA grease used by the military.

3. Aircraft Arresting Cables

The Naval Air Engineering Center, Lakehurst, NJ, is evaluating greases containing $SbSbS_4$ on arresting cables used on aircraft carriers. Major improvements including longer cable lives and less slippery decks are sought. This application study is sponsored by NAEC (contract N68335-81-C-5280); however, the ONR program provides the necessary basic technical underpinning.

4. Toxicology

Because greases containing $SbSbS_4$ have advanced to the field test stage, we have obtained acute oral and dermal toxicity data on this compound which indicate that it is nontoxic. All animals survived at an oral dose of 5 g/kg (rats) and a dermal dose of 2 g/kg (rabbits), were normal clinically, and gained weight throughout this study. Skin and eye irritation tests also indicate that the compound is substantially benign. Arrangements have been made with the Naval Medical Research & Development Command for a 90-day subchronic dermal study which is expected to be completed by early 1983.

D. CERIUM OXYTHIOMOLYBDATES

1. General

Numerous attempts to prepare cerium thiomolybdate, $Ce_2(MoS_4)_3$, gave products with elemental analysis corresponding to cerium oxythiomolybdate complexes, $Ce_2(MoO_xS_{4-x})_3 \cdot nH_2O$, where x = 1-3. These complexes were evaluated for lubricant properties in a lithium base grease and found to exhibit good antiwear properties on both chrome tool and stainless steels. These results prompted our further study of the synthesis, character-

ization, and evaluation of cerium oxythiomolybdate complexes. A number of reactions were carried out using three different routes but in all cases the reaction products were found to be non-stoichiometric. It was not clear whether this non-stoichiometry reflected the particular nature of complex sulfides involving cerium and molybdenum or was due to lack of suitable reaction conditions. The three reaction routes, the resulting compositions, and their performance as lubricant additives are summarized below.

2. Reaction of ammonium molybdate with hydrogen sulfide

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O + nH_2S \longrightarrow (NH_4)_2MoO_xS_{4-x} + \text{by-products}$$
$$3(NH_4)MoO_xS_{4-x} + 2CeCl_3\cdot 7H_2O \longrightarrow Ce_2(MoO_xS_{4-x})_3\cdot nH_2O + \text{by-products}$$

Analysis of the cerium complex reaction products showed variable ratios of sulfur to cerium depending on the particular experiment. A large supply of cerium complex, prepared by the above reaction sequence for detailed evaluation and characterization, approximated $Ce_2(MoO_{1.2}S_{2.8})_3\cdot 6H_2O$ by elemental analysis. The material was found to be amorphous by X-ray diffraction.

Tables I through IV summarize the performance data of $Ce(MoO_{1.2}S_{2.8})_3\cdot 6H_2O$ as a lubricant additive at various concentrations primarily in a lithium grease. For reference purposes, the lubricating properties of greases containing 5% MoS_2 are also listed. On chrome tool steel 52100 the weld point of the base grease containing 5% cerium complex is comparable to that of the grease containing MoS_2; however, the load wear index and wear prevention characteristics of the grease containing the cerium complex are definitely superior (Table I). On stainless steel 440-C the grease containing 5% cerium

complex again shows superior antiwear characteristics and comparable extreme pressure properties to those of molybdenum disulfide.

A lithium grease containing a mixture of 1% $SbSbS_4$ and 1% $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$ was also evaluated. The objective of this experiment was to see whether such a combination could impart both extreme pressure and antiwear properties to the base grease at a low level of additive concentration. The results are recorded in Tables I, II, and III and show that this combination at a total concentration level of 2% greatly improves the EP and antiwear properties of base grease.

The concentration effect (0.1 to 5%) of the cerium complex in a lithium grease on the wear prevention characteristics is shown in Table IV. The scar diameters on chrome tool steel are quite small and do not show much concentration dependence as indicated by very little change in the wear scar diameters of the greases containing 0.5 to 5% of the cerium complex. In the case of stainless steel, there is a definite trend of increasing wear scar diameters with decreasing concentration of the cerium complex.

The cerium complex was also evaluated in an aluminum complex grease. The Shell Four-Ball weld points and load wear indices of this grease containing 5% MoS_2 and 5% $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$ are recorded in Table I. It appears that the cerium complex shows slightly superior EP performance to MoS_2.

3. Reaction of Sodium Molybdate with Sodium Sulfide

$$Na_2MoO_4 \cdot 2H_2O + 3Na_2S \longrightarrow Na_2MoO_xS_{4-x} + \text{by-products}$$
$$3Na_2MoO_xS_{4-x} + 2CeCl_3 \cdot 7H_2O \longrightarrow Ce(MoO_xS_{4-x})_3 \cdot nH_2O + \text{by-products}$$

Because of difficulties encountered in controlling the flow of hydrogen sulfide in the reaction with ammonium molybdate, sodium molybdate was treated with sodium sulfide to produce a solution of sodium oxythiomolybdate. The sodium oxythiomolybdate solution was then treated with a cerium trichloride solution at different pH ranges. None of the product analyses correspond to the expected cerium to molybdenum ratio. No additional work on this reaction was carried out.

4. Reaction of Sodium Molybdate with Cesium Acetate

$$Na_2MoO_4 \cdot 2H_2O + CsOAc \xrightarrow{H_2S} Cs_2MoOS_3 + \text{by-products}$$
$$3Cs_2MoOS_3 + 2CeCl_3 \cdot 7H_2O \longrightarrow Ce_2(MoOS_3)_3 + \text{by-products}$$

The synthesis of cesium oxythiomolybdate, Cs_2MoOS_3, was carried out as reported in the literature[5] by reaction of cesium acetate with sodium molybdate followed by passing hydrogen sulfide through the reaction mixture at pH 10.

Attempts were then made to prepare $Ce_2(MoOS_3)_3 \cdot nH_2O$ starting from Cs_2MoOS_3. In our first attempt, an aqueous solution of $CeCl_3 \cdot 7H_2O$ was added to an aqueous solution of Cs_2MoOS_3 in 2:3 molar ratio at room temperature. A light brown solid was isolated (about 50% yield) whose analysis (Ce:Mo:S = 2:2.2:5.7) did not correspond to the expected composition, $Ce_2(MoOS_3)_3 \cdot nH_2O$. However, its extreme pressure and antiwear properties in a lithium grease are superior to those of the sample obtained from ammonium oxythiomolybdate (Figure I).

5. Thermogravimetric Analysis of Cs_2MoOS_3 and Selected Samples of Cerium Oxythiomolybdate Complexes

a. Cesium Oxythiomolybdate - Cs_2MoOS_3

Thermogravimetric analysis of cesium oxythiomolybdate was carried out both in air and nitrogen at a heating rate of 5°C/minute. This product was selected for thermal study because it has a well defined composition and, therefore, it can provide information on the expected thermal stability of complexes containing the $MoOS_3^{-2}$ anion. As shown in Figure II, the material is remarkably stable both in air and nitrogen. With the exception of a slight weight loss of about 2% at 280°C followed by gradual weight gain of up to 4% around 410°C in air, there is no change until 600°C. Under nitrogen, there is essentially no change in weight up to 600°C; a very slight deflection showing less than 2% weight loss between 300 and 500°C may be attributed to the presence of impurities.

b. Cerium Oxythiomolybdate Complexes Prepared by Different Methods

Two samples of cerium oxythiomolybdate complexes prepared from ammonium oxythiomolybdate and cesium oxythiomolybdate, respectively, were selected for thermal study in air. The TGA curves are shown in Figure III. The initial weight loss up to 300°C for both samples may be attributed to water and this appears to be consistent with the elemental analysis. The two samples show different modes of decomposition with increasing temperatures. The complex prepared from Cs_2MoOS_3 shows weight gain from 400 to 600°C whereas the complex prepared from ammonium

oxythiomolybdate shows a slight weight gain between 350 and 380°C, followed by a weight loss of about 8% from 380 to 450°C. Both complexes appear to be stable up to 400°C in air after dehydration.

E. ZINC THIO- AND OXYTHIOMOLYBDATES

1. General

Synthesis and characterization of three stoichiometric zinc thio- and oxythiomolybdates - $ZnMoS_4 \cdot 3H_2O$, $ZnMoOS_3 \cdot 3H_2O$, and $ZnMoO_2S_2 \cdot 3H_2O$ - and their corresponding anhydrous compositions, was more successful. The compositions showed considerable promise as antiwear additives especially for high temperature use on stainless steel. For example, $ZnMoO_2S_2$ was found to be much superior to MoS_2 as an extreme pressure and antiwear additive in lithium grease and was stable in air up to 400°C (750°F).

The following sections describe the synthetic procedures for these compositions. Table V lists the performance data of both hydrated and anhydrous zinc complexes. The thermogravimetric analysis of $ZnMoO_2S_2$ in air is shown in Figure IV.

2. Preparation of $ZnMoS_4 \cdot 3H_2O$ and $ZnMoS_4$

$$ZnCl_2 + (NH_4)_2MoS_4 \xrightarrow{\text{in } H_2O} ZnMoS_4 \cdot 3H_2O + 2NH_4Cl$$

$$ZnMoS_4 \cdot 3H_2O \xrightarrow[\text{in N}]{350°C/2hrs} ZnMoS_4 + 3H_2O$$

A sample of 5.0 g $(NH_4)_2MoS_4$ (prepared as described in the literature[6]) was dissolved in 100 ml distilled water. The resulting solution was slowly added with an aqueous solution of $ZnCl_2$ (2.6 g in 20 ml distilled water). A black solid formed immediately. The reaction

mixture was then stirred for two hours at room temperature and filtered. The solid product was washed with acetone and dried at 110°C for four hours (5.3 g or 75% yield). X-ray diffraction indicated that this material was amorphous.

Calculated for $ZnMoS_4 \cdot 3H_2O$: Zn, 19.0; Mo, 27.9; S, 37.3
Found: Zn, 19.6; Mo, 28.6; S, 37.9

The anhydrous material was prepared as indicated above.

3. Preparation of $ZnMoO_2S_2 \cdot 3H_2O$ and $ZnMoO_2S_2$

$$ZnCl_2 + (NH_4)_2MoO_2S_2 \xrightarrow{\text{in } H_2O} ZnMoO_2S_2 \cdot 3H_2O + 2NH_4Cl$$

$$ZnMoS_4 \cdot 3H_2O \xrightarrow[\text{in } N_2]{350°C/2hrs} ZnMoO_2S_2 + 3H_2O$$

An aqueous solution of $ZnCl_2$ (5.38 g in 50 ml distilled water) was slowly added to a solution of $(NH_4)_2MoO_2S_2$ (9.0 g in 100 ml distilled water; the compound was prepared as described in the literature[6,7]) resulting in slightly exothermic reaction. A dark brown solid formed immediately. The reaction mixture was stirred for one hour at room temperature and then filtered. The black solid was washed with distilled water and dried at 110°C for three hours (6.6 g or 66% yield). X-ray diffraction indicated that this solid was amorphous.

Calculated for $ZnMoO_2S_2 \cdot 3H_2O$: Zn, 21.0; Mo, 30.8; S, 20.6
Found: Zn, 23.9; Mo, 29.8; S, 23.4

The anhydrous material was prepared as indicated above.

4. Preparation of $ZnMoOS_3 \cdot 3H_2O$ and $ZnMoOS_3$

$$Cs_2MoOS_3 + ZnCl_2 \xrightarrow{\text{in } H_2O} ZnMoOS_3 \cdot 3H_2O + 2CsCl$$

$$ZnMoOS_3 \cdot 3H_3O \xrightarrow[\text{in } N_2]{350°C/2hrs} ZnMoOS_3 + 3H_2O$$

A solution of 15.4 g $Cs_2(MoOS_3)$ (prepared as described in the literature[5]) in 100 ml distilled water was treated with a $ZnCl_2$ solution (4.4 g in 30 ml distilled water). The reaction mixture was reflexed for 1.5 hrs. A brown solid deposited. The solid product was isolated by filtration, washed twice with distilled water and dried at 105°C for three hours (10.2 g). X-ray diffraction indicated that this solid was amorphous.

Calculated for $Zn(MoOS_3) \cdot 3H_2O$:	Zn, 20.0; Mo, 29.3; S, 29.3
Found:	Zn, 23.4; Mo, 30.1; S, 29.2

The anhydrous material was prepared as indicated above.

5. Toxicology

Some toxicology tests were carried out on $ZnMoO_2S_2 \cdot 3H_2O$ with favorable results, as follows:

Skin irritation test: Non irritating

Eye irritation test: Mildly irritating without washout

Acute dermal LD50 (rabbits) >2g/kg

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G. ACKNOWLEDGEMENT

We would like to acknowledge the many scientific contributions of Mr. M. J. Devine who has provided support of the highest professional level at the request of ONR and especially for his attention to requirements of the U. S. Marine Corps for amphibious and desert operations.

Table I. Shell Four-Ball Weld Points and Load Wear Indices[1] of Cerium Oxythiomolybdate[2] in Lithium and Aluminum Complex Greases on Chrome Tool Steel Balls (AISI-52100)

Grease Composition	Weld Point kg	Scar Diameter Before Weld mm (kg)	Load Wear Index
Lithium Grease	140	2.64(126)	18.3
Lithium Grease + 5% MoS_2	250	2.90(224)	30.4
Lithium Grease + 5% Cerium Complex	250	2.02(200)	41.4
Lithium Grease + 1% $SbSbS_4$ + 1% Cerium Complex	400	1.61(315)	59.5
Aluminum Complex Grease (ACG)	100	2.10(70)	11.8
ACG + 5% MoS_2	190	2.24(160)	35.5
ACG + 5% Cerium Complex	200	2.10(160)	40.2

1. ASTM-D-2596
2. $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$

Table II. Shell Four-Ball Weld Point and Load Wear Index[1] of Cerium Oxythiomolybdate[2] in Lithium Grease on Stainless Steel Balls (AISI-440C)

Grease Composition	Weld Point kg	Load Wear Index
Lithium Grease	80	3.5
Lithium Grease + 5% MoS_2	100	6.1
Lithium Grease + 5% Cerium Complex	100	10.4
Lithium Grease + 1% $SbSbS_4$ and 1% Cerium Complex	140	11.8

1. ASTM-D-2596
2. $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$

Table III. Shell Four-Ball Wear Prevention Characteristics[1] of Lithium Grease Containing Additives on Chrome Tool Steel Balls (AISI-52100) and Stainless Steel Balls (AISI-440C)

Grease Composition	Wear Scar Diameter on 52100 Balls mm	Wear Scar Diameter on 440-C Balls mm
Lithium Grease	0.70	3.96
Lithium Grease + 5% MoS_2	0.65	2.34
Lithium Grease + 5% Cerium Complex[2]	0.40	1.38
Lithium Grease + 1% $SbSbS_4$ and 1% Cerium Complex[2]	0.43	0.84

1. ASTM-D-2266 - 1200 rpm, 167°F, 40 kg for one hour
2. $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$

Table IV. Effect of Concentration of $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$ in Lithium Grease on Wear Scar Diameters[1]

Grease Composition	Wear Scar Diameter on 52100 Steel Balls mm	Wear Scar Diameter on S.S. 440C Balls mm
Lithium Grease	0.70	3.96
Lithium Grease + 0.1% Cerium Complex	0.59	2.64
Lithium Grease + 0.5% Cerium Complex	0.39	2.47
Lithium Grease + 1% Cerium Complex	0.40	2.26
Lithium Grease + 3% Cerium Complex	0.40	1.84
Lithium Grease + 5% Cerium Complex	0.41	1.38

1. ASTM-D-2266 - 1200 rpm, 167°F, 40 kg for one hour

Figure I. Wear Scar Diameter vs. Load
(52100 Steel Balls; 25°C, 1800 rpm, 10 sec.)

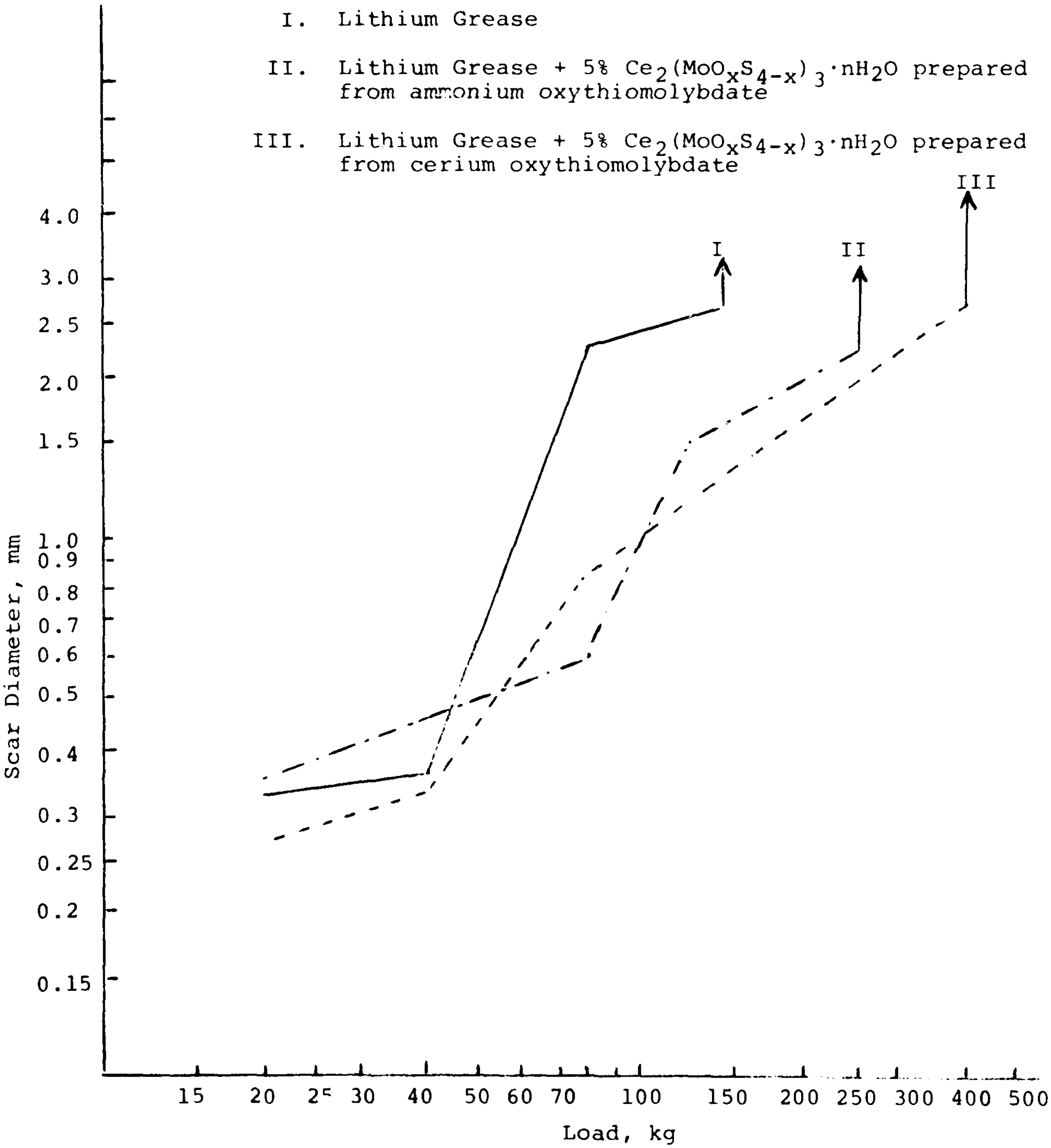


Figure II. Thermogravimetric Analysis of Cs_2MoOS_3 in Air and Nitrogen

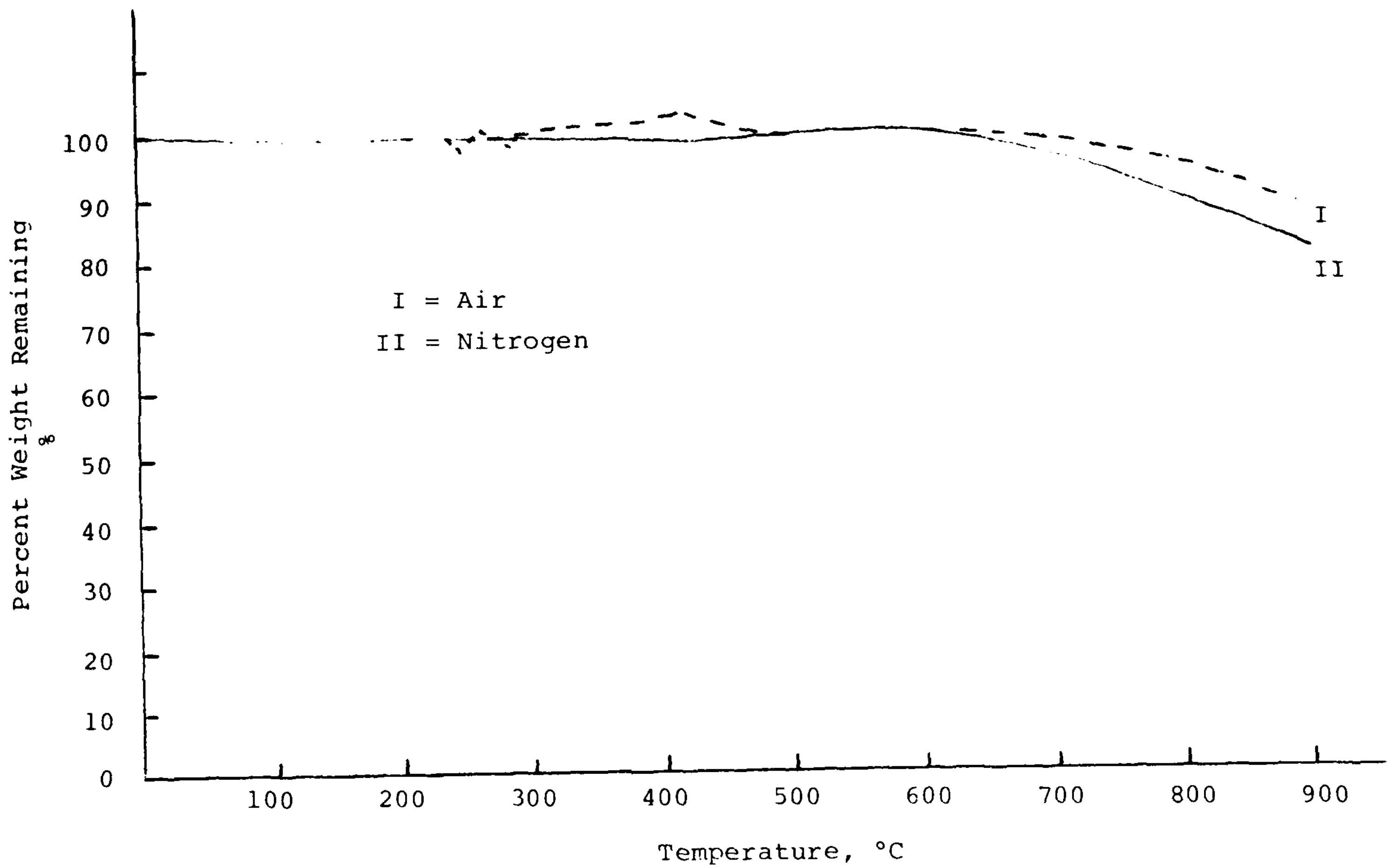


Figure III. Thermogravimetric Analysis in Air of Cerium Oxythiomolybdate Complexes Prepared By Two Different Methods

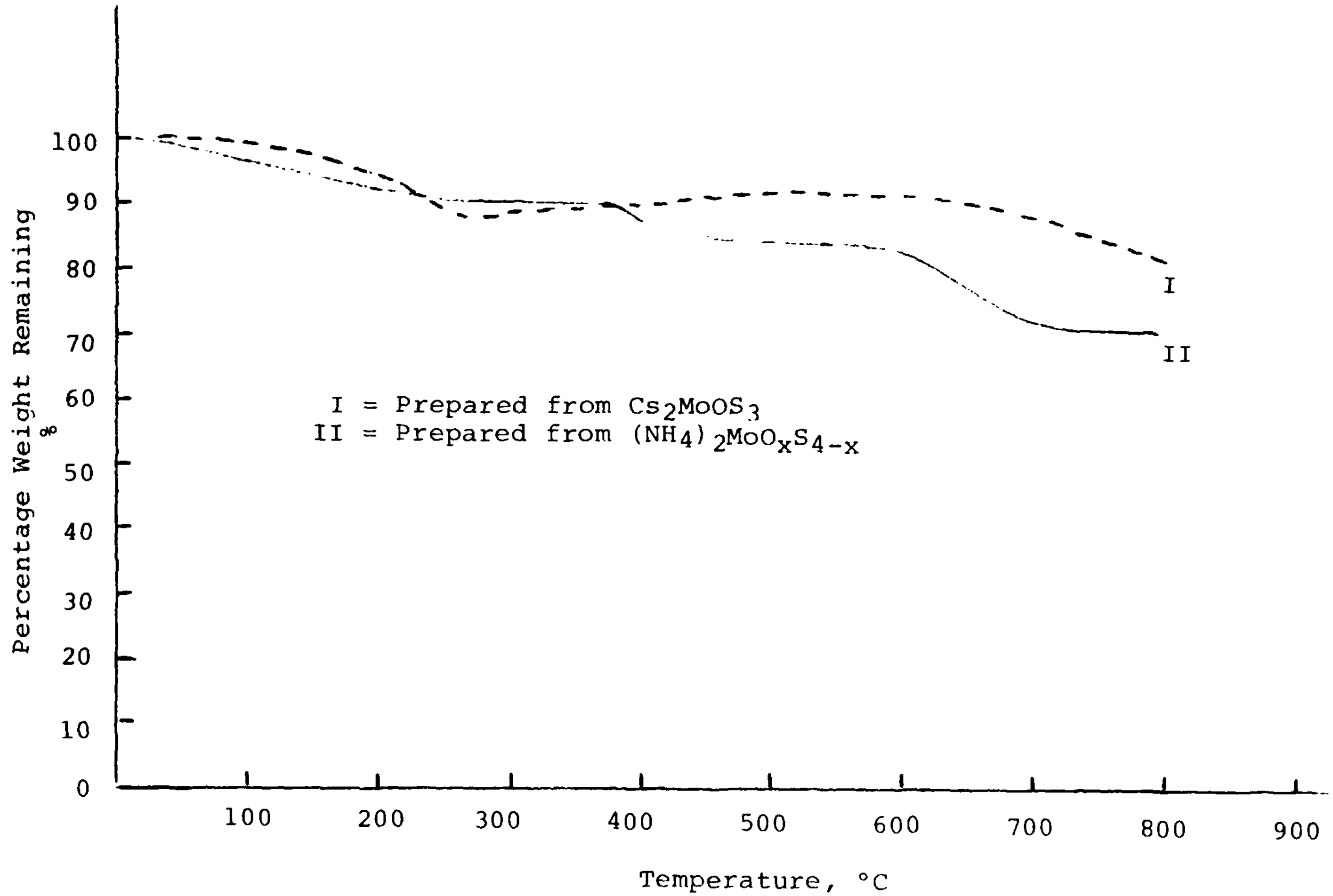
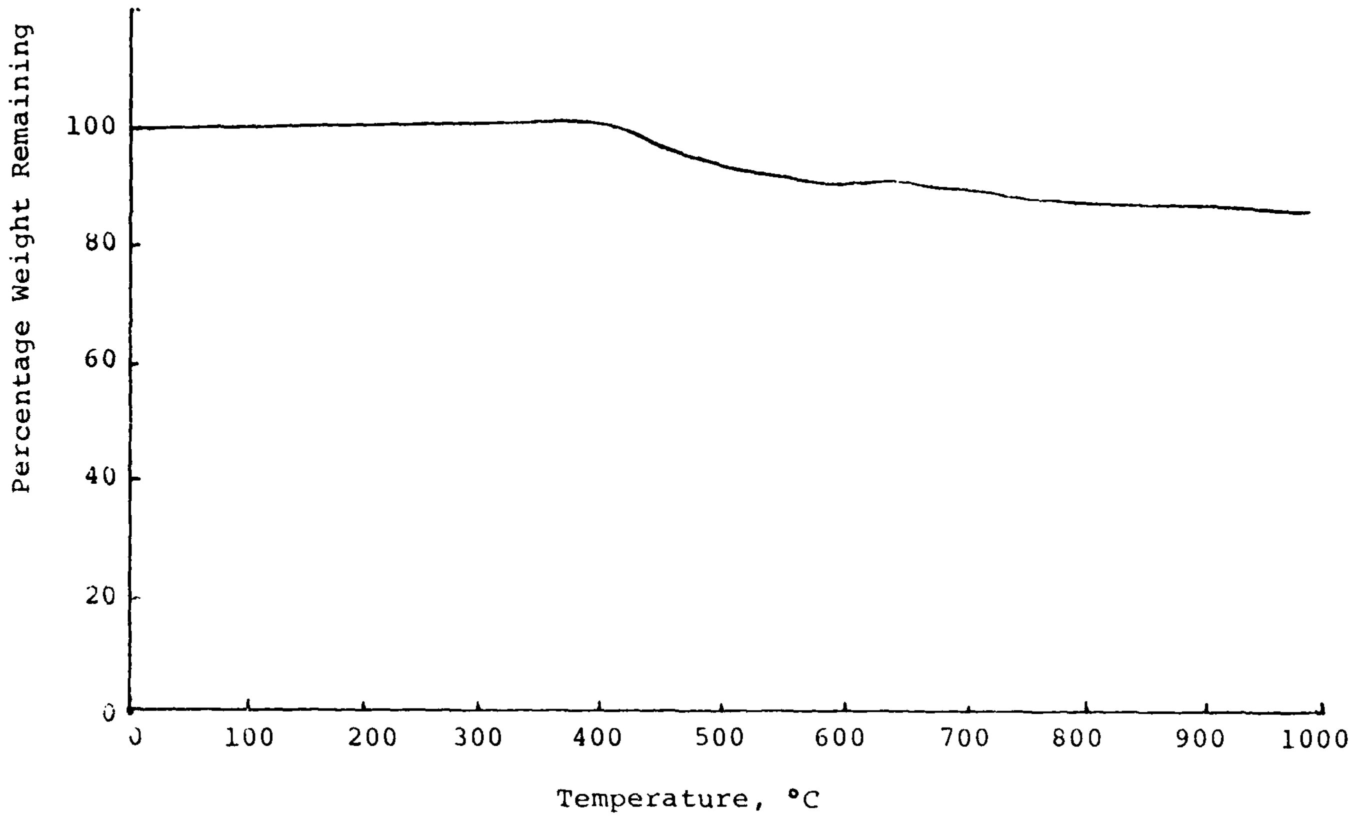


Table V. Lubricant Properties of Thio- and Oxythiomolybdate Complexes

Grease Composition	Weld Pt. kg	LWI[a]	Wear Scar Diameter, MM[b] Before Dehydration 52100	Before Dehydration SS 440	After Dehydration[b] 52100	After Dehydration[b] SS 440
Lithium Grease (L.G.)	140	18.3	0.70	3.96	---	---
L.G. + 5% MoS_2	250	80.4	0.65	2.34	---	---
L.G. + 5% $ZnMoS_4 \cdot 3H_2O$	250	37.4	0.42	0.44	0.38	0.38
L.G. + 5% $ZnMoOS_3 \cdot 3H_2O$	315	52.0	0.44	0.53	0.50	1.50
L.G. + 5% $ZnMoO_2S_2 \cdot 3H_2O$	315	60.6	0.40	0.84	0.48	0.61

a. 1200 rpm, 167°F, and 40 kg for 1 h.
b. The zinc complexes were dehydrated under N_2 at 350°C for two hours.

Figure IV. Thermogravimetric Analysis of $ZnMoO_2S_2$ in Air



APPENDIX I

VOLUME 24, 4, 497–504
ASLE TRANSACTIONS

Investigation of Extreme-Pressure and Antiwear Properties of Antimony Thioantimonate

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Detailed studies including synthesis, characterization and evaluation of antimony thioantimonate, $SbSbS_4$, have been carried out. The amorphous complex chalcogenide was prepared by a solution precipitation method. As a solid lubricant additive in various greases, this material exhibits superior extreme pressure and antiwear properties as demonstrated by the Four Ball weld points and load wear indexes on both AISI 52100 and AISI 440C steels. Antimony thioantimonate appears to be compatible with all the base greases investigated including a silicone grease in which very few additives show good response.

INTRODUCTION

Continuing advances in technology require the development of lubricant systems capable of meeting the challenge presented by increasing speeds, high loads and extremes of temperature. Lubricants may also be required to function in high vacuum or corrosive environments and to exhibit broad response to various metals and alloys. There is a crucial need for effective solid lubricants in aircraft, ship, mining and oil drilling equipment, and space vehicle parts to lower friction, prevent contact surfaces from welding and reduce energy requirements. The solid lubricants commonly used for these purposes are graphite and molybdenum disulfide. The use of graphite as solid lubricant has certain drawbacks in some applications because of limitations such as galvanic corrosion, necessary presence of water vapor or hydrocarbon in order to be effective and unsatisfactory performance in vacuum. Molybdenum disulfide is in short supply. There are few solid lubricants available today that can function properly under high load. It is, therefore, essential that effective replacements for these materials be found and made available.

A number of complex metal chalcogenides previously synthesized were examined (*1*), (*2*), (*3*), (*4*) for their performance as extreme-pressure and antiwear additives in greases, solid-film lubricants and fluids. As extreme-pressure and antiwear additives, these complex chalcogenides were superior to simple sulfides, including MoS_2. One composition, arsenic thioantimonate—which was well characterized and evaluated (*2*)—was found to be an outstanding solid lubricant. When the safety of all inorganic arsenic compounds came under question, development of arsenic thioantimonate was terminated.

A study was then undertaken to determine the potential of antimony thioantimonate, $SbSbS_4$, as a solid-lubricant additive. This report covers investigation of the lubricating properties of $SbSbS_4$ in various greases. Of particular interest is the development of a lubricant effective for use with chrome tool and stainless steels.

Experimental

Preparation of Antimony Thioantimonate

Antimony thioantimonate was prepared from aqueous solution by a precipitation procedure similar to that used to prepare arsenic thioantimonate (*1*). An alkaline solution of Sb_2O_3 was added to an aqueous solution of sodium thioantimonate ($Na_3SbS_4 \cdot 9H_2O$). The resulting solution was filtered to remove a small amount of $NaSb(OH)_6$, and the filtrate was slowly neutralized with a phosphoric acid solution under nitrogen atmosphere. (Hydrochloric or sulfuric acid could also be used.) A precipitate was formed, filtered, washed several times with distilled water, alcohol, acetone, and carbon tetrachloride, and dried in vacuo at 75°C. to constant weight. Sodium thioantimonate solution was prepared by refluxing a mixture of sodium sulfide, sulfur and antimony trisulfide (3:1.05:1 molar ratio) in an aqueous medium under a nitrogen atmosphere. After most of the sulfur had disappeared, the reaction product was filtered to remove the excess sulfur, and the filtrate was combined with an alkaline solution of antimony oxide. The overall reaction may be represented as follows:

$$Sb_2O_3 + 2KOH + 2Na_3SbS_4 + 8H^+ \longrightarrow 2SbSbS_4 + 2K^+ + 6Na^+ + 5H_2O$$

Presented as an American Society of Lubrication Engineers paper at the ASME/ASLE Lubrication Conference in San Francisco, California, August 18–21, 1980.

The antimony trisulfide of 97-percent purity and the molybdenum disulfide was of technical grade.

Selection of Base Greases

Four base greases representing a broad spectrum of the industrial greases used today were selected for use in evaluating antimony thioantimonate. Test samples were prepared by mixing appropriate amounts of additive and grease (expressed in wt. percent) on a three-roll mill for 3–5 passes. Details of the base greases are given in Table 1.

Test Methods

Four Ball Testers

The extreme-pressure and antiwear properties of the greases were determined on Shell Four-Ball EP and Wear Testers. These testers provide for sliding steel vs steel (AISI-52100 vs AISI-52100 and AISI-440C vs AISI-440C) with spherical specimens. Weld points and load wear indexes were determined in a series of runs (10 s, 1800 rpm, 77 F) conducted at various loads, and scar diameters were measured after each run in accordance with ASTM D 2596. Wear prevention characteristics were determined by measuring scar diameters of test specimens after each run at 1200 rpm, 40 kg, 167 F for one hour. This test is described in ASTM D 2266.

Falex Machine

The load-carrying capacities of certain selected grease samples were measured on a Falex machine using AISI-C-3135 steel pins and AISI-C-1137 V-blocks. The testing procedure is similar to ASTM D 3233.

Oxidation Test

Antioxidant properties of some greases were determined in an oxidation bomb under pure oxygen at 210 ± 2 F for 100 h. Relative antioxidant ability was rated by measuring the drop in oxygen pressure after 100 h. This test is described in ASTM D 942.

Copper Corrosion

A copper strip was allowed to remain in contact with the lubricating grease containing the complex sulfide for a period of 24 h at a specified temperature. After the exposure was completed, the surface of the copper specimen was examined for discoloration, etching, pitting, or other signs of corrosion. This procedure is similar to the method outlined in 5309.2 of FTMS No. 791a.

Characterization of Antimony Thioantimonate

Antimony *thioantimonate* is a reddish-brown solid insoluble in most organic solvents and mineral acids. It is soluble in alkali and is amorphous by X-ray diffraction. A typical sample analyzed 65.5 percent Sb and 33.2 percent S (Calc'd Sb 65.5 percent and 34.5 percent S). The density determined at 23°C is 3.55 g/cc. The thermal stability of $SbSbS_4$ has been investigated by thermogravimetric analysis. When $SbSbS_4$ is heated in air at 9°F/min, there is *approximately* 8-percent weight loss between 380 F and 700 F, and the rate of weight loss does not become rapid with increasing temperature until 840 F is exceeded. At 750 F, 90 percent of the compound remained under these dynamic heating conditions. Antimony *thioantimonate* is a potential candidate for moderate-to high-temperature solid-lubricant applications. A TGA curve is presented in Figure 1. To further verify the composition and characterize the material, it was heated in a *nitrogen atmosphere*. It was found to melt at *about* 510°C. After being held at 525°C for 36 h, the sample had lost 9.1 percent of its original weight, which closely approaches the theoretical weight loss for conversion *of* Sb_2S_5 to Sb_2S_3, and the resulting product was identified as crystalline Sb_2S_3 by X-ray diffraction analysis.

Results and Discussion

Lubricating Properties of $SbSbS_4$ on Chrome Tool Steel AISI-C-52100

The properties of antimony thioantimonate as an antiwear and extreme-pressure additive in various greases were evaluated on Shell Four-Ball EP and Wear Testers using both chrome-tool and stainless-steel balls. For reference purposes, the lubricating properties of 5-percent molyb-

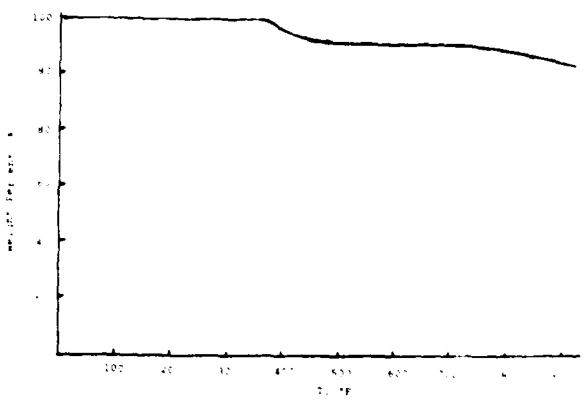

Fig. 1—*Thermogravimetric* analysis of $SbSbS_4$ in air

TABLE 1—TYPES OF BASE GREASES* INVESTIGATED

GREASE	THICKENER (%)	FLUID
A. Lithium Grease	Lithium 12-OH Stearate (6)	Naphthenic mineral oil
B. Clay Grease	Clay (5)	Paraffinic mineral oil
C. Silicone Grease	Lithium Stearate (12)	Methylphenyl silicone
D. Aluminum Complex Grease	Aluminum Complex (7.5)	Paraffinic mineral oil

*No other chemical agents were included in these greases so the effect of specific additives could be determined.

denum disulfide in the same base greases were also determined. The weld points and wear load indices with chrome tool steel balls (AISI-52100) were determined for base greases, base greases containing 5-percent antimony thioantimonate, and base greases containing 5-percent MoS_2. The results are recorded in Table 2 along with the scar diameters before weld. At 5-percent concentration, antimony thioantimonate ($SbSbS_4$) has antiwear and EP properties superior to those of molybdenum disulfide. In fact, even the 1-percent $SbSbS_4$ grease outperformed the 5-percent MoS_2 grease. A graphical comparison of the data obtained in a lithium grease is presented in Fig. 2.

The wear prevention characteristics of the four base greases, and the same greases containing either 5-percent $SbSbS_4$ or 5-percent MoS_2, were determined on a Four-Ball Wear Tester at 40 kg, 167 F, 1200 rpm for one hour. The results for 52100 steel vs 52100 steel and 440C stainless steel vs 440C stainless steel are recorded in Table 3. The wear prevention characteristics with Chrome-steel balls (AISI 52100) showed a slight improvement for the greases containing $SbSbS_4$ and MoS_2 over the corresponding base greases in most cases. There is no significant difference in antiwear properties at 40-kg load between $SbSbS_4$ and MoS_2 in all four greases.

The effect of antimony thioantimonate concentration on the lubricating properties of a lithium grease was investigated. The weld points and load-wear indices of a lithium grease containing 0.5 to 5.0-percent antimony thioantimonate were determined. For comparison, the weld points and load-wear indexes of the same base grease containing 1 to 5-percent MoS_2 were also obtained. The results are listed in Table 4. These results suggest that high-performance EP greases can be formulated with considerably lower concentrations of $SbSbS_4$ than of MoS_2. The results of various properties of lithium grease containing 5-percent $SbSbS_4$ and 5-percent MoS_2 are recorded in Table 5.

A lithium grease containing different extreme-pressure additives including both inorganic and organometallic compounds, was investigated. The load wear indixes of the same base grease containing various additives were determined. The results are presented in Fig. 2. Again, the superior extreme-pressure properties of antimony thioantimonate were demonstrated.

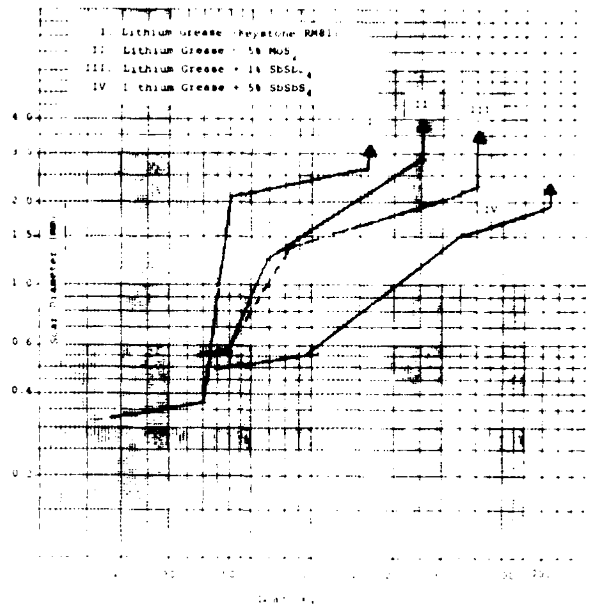

Fig. 2—Wear scar diameter vs load; AISI-C-52100 steel balls; 25°C, 1800 rpm, 10 s.

Preliminary evaluation of the load-carrying properties of various base greases containing antimony thioantimonate ($SbSbS_4$) and MoS_2 were carried out on a Falex machine. The results are recorded in Table 6.

Lubricating Properties of $SbSbS_4$ on Stainless-Steel AISI-440C

In general, corrosion-resistant metals or alloys are diffi-

TABLE 2—WELD POINTS AND LOAD WEAR INDICES* OF ANTIMONY THIOANTIMONATE IN VARIOUS GREASES

	Weld Point kg	Scar Diameter Before Weld mm(kg)	Load Wear Index
Lithium Grease	140	2.64 (126)	18.3
Lithium Grease + 5% MoS_2	250	2.90 (224)	30.4
Lithium Grease + 1% $SbSbS_4$	400	2.38 (315)	43.0
Lithium Grease + 5% $SbSbS_4$	760	2.20 (710)	98.3
Silicone Grease	126	2.17 (100)	15.7
Silicone Grease + 5% MoS_2	190	1.44 (160)	33.1
Silicone Grease + 5% $SbSbS_4$	560	1.96 (500)	74.9
Clay Grease	200	2.74 (180)	26.2
Clay Grease + 5% MoS_2	250	2.72 (224)	38.8
Clay Grease + 5% $SbSbS_4$	560	1.86 (500)	78.1
Aluminum Complex Grease	100	2.10 (70)	11.8
Aluminum Complex Grease + 5% MoS_2	190	2.24 (160)	35.5
Aluminum Complex Grease + 5% $SbSbS_4$	448	2.02 (400)	83.7

*ASTM D2596—AISI 52100 steel balls

TABLE 3—SHELL FOUR-BALL WEAR PREVENTION CHARACTERISTICS* OF GREASES CONTAINING ADDITIVES ON CHROME TOOL AISI C-52100 AND STAINLESS AISI-C-440 STEELS

Grease Composition	Wear Scar Diameter on AISI-C-52100 Balls (mm)	Wear Scar Diameter on AISI-440C Balls (mm)
Lithium Grease	0.70	3.96
Lithium Grease + 5% $SbSbS_4$	0.63	0.78
Lithium Grease + 5% MoS_2	0.65	2.34
Silicone Grease	1.99	—
Silicone Grease + 5% $SbSbS_4$	2.11	—
Silicone Grease + 5% MoS_2	2.11	—
Clay Grease	0.69	—
Clay Grease + 5% $SbSbS_4$	0.65	0.57
Clay Grease + 5% MoS_2	0.64	0.84
Aluminum Complex Grease	0.65	2.27
Aluminum Complex Grease + 5% $SbSbS_4$	0.65	1.14
Aluminum Complex Grease + 5% MoS_2	0.63	2.59

*ASTM D 2266

cult to lubricate, especially under high load conditions. In many applications, the use of corrosion-resistant alloys is limited by severe wear problems. The lubricating properties of four different greases containing 5-percent $SbSbS_4$ have been evaluated with AISI-440C stainless-steel balls in a Shell Four-Ball EP Tester. For comparison, the lubricating properties of the same greases containing 5-percent molybdenum disulfide have also been determined on AISI-440C. At 5-percent concentration of $SbSbS_4$ in four greases, the weld points of stainless-steel balls showed improvements of 100 to 400 percent over the same greases containing 5-percent molybdenum disulfide. Experimental results are given in Table 7. The scar diameter vs load graphs shown in Fig. 4 and 5 indicate that the greases containing $SbSbS_4$ exhibit excellent response to stainless steel. Stainless steel is difficult to lubricate, and there are very few additives that can impart good response to silicone greases as confirmed by the results obtained on the silicone grease containing 5-percent MoS_2 (see Fig. 5). It is significant that the extreme-pressure properties of the silicone grease containing 5-percent $SbSbS_4$ are greatly improved over those of the base grease and the base grease containing 5-percent MoS_2.

The wear prevention characteristics of 5-percent $SbSbS_4$ in three greases—lithium, clay and aluminum complex greases—were determined on a Shell Four-Ball Wear Tester using AISI 440C (stainless steel) balls. The scar diameters for the lithium grease and the lithium grease containing 5-percent MoS_2 were 400 and 300 percent larger than for the same base grease containing 5-percent $SbSbS_4$. In fact, the wear scar diameter of the lithium grease containing 5-percent $SbSbS_4$ on AISI-440C stainless-steel balls was only slightly larger than the wear scar obtained for the same grease on AISI-52100 balls (0.78 vs 0.63 mm). For 5-percent concentration of MoS_2 in a silicone grease, the wear scar diameter was larger than that for the base grease (2.59 vs 2.27 mm). However, the presence of 5-percent $SbSbS_4$ in the same silicone grease resulted in 100-percent improvement over the base grease (see wear data in Table 3).

Table 8 lists the comparative wear scar diameters of both AISI-52100 and AISI-440C balls obtained for the same base greases under different loads. The differences in performance between MoS_2 and $SbSbS_4$ in different greases on both chrome and stainless steel are quite obvious. The results in Table 8 also indicate that the use of MoS_2 on stainless-steel balls is quite limited. The good performance of $SbSbS_4$ on various alloys and in a variety of greases has been quite universal. It is interesting to note that lithium grease containing 5-percent $SbSbS_4$ gives smaller wear scar diameters on AISI-440C stainless-steel balls under a given applied load and a higher weld point than the same grease containing 5-percent MoS_2 on chrome-tool steel.

CONCLUSION

Antimony thioantimonate incorporated into different greases as a solid additive at low concentration imparts outstanding extreme-pressure properties both on chrome tool and stainless steels. At lower loads, the wear prevention characteristics on tool steel in various greases are comparable to molybdenum disulfide; however, the wear prevention characteristics of antimony thioantimonate on stainless steel in different greases showed considerable improvement over molybdenum disulfide. In general, antimony thioantimonate showed excellent response toward both tool and stainless steels in a variety of greases, including a silicone grease with which very few solid lubricants are compatible. Antimony thioantimonate is a candidate solid-lubricant ad-

TABLE 4—PERFORMANCE OF LITHIUM GREASE CONTAINING DIFFERENT CONCENTRATIONS OF $SbSbS_4$ AND MoS_2 ON CHROME-TOOL STEEL AISI-52100

Grease Composition	Weld Point (kg)	Load-Wear Index
Lithium Grease	140	18.3
Lithium Grease + 0.5% $SbSbS_4$	200	25.8
Lithium Grease + 1% $SbSbS_4$	400	43.0
Lithium Grease + 1% MoS_2	126	17.6
Lithium Grease + 3% $SbSbS_4$	620	57.0
Lithium Grease + 3% MoS_2	162	26.5
Lithium Grease + 5% $SbSbS_4$	760	98.4
Lithium Grease + 5% MoS_2	250	30.4

TABLE 5—ANTIMONY THIOANTIMONATE PERFORMANCE IN LITHIUM GREASE

PROPERTIES	LITHIUM GREASE	LITHIUM GREASE + 5% $SbSbS_4$	LITHIUM GREASE + 5% MoS_2
Penetration (ASTM D 217)			
Unworked	253	315	...
Worked, 60 strokes	285	269	
Drop point (ASTM D 566) °F	365	369	370
Oxidation Stability (ASTM D 942)			
Psig O_2 pressure drop in 100 hours 210°F	10	7	34
Lubrication Properties			
Extreme-pressure properties (ASTM D 2596)*		—	.
Load wear index	18.3	98.3	30.4
Weld point, kg	160	760	250
Wear prevention characteristics (ASTM D 2266)* 40 kg load, 1 hour, 1200 rpm at 167°F	0.70	0.63	0.65
Falex E.P. lbs (ASTM D 3233)†	< 300	2250	1850
Copper Corrosion 24h at 212°F	pass	pass‡	pass

*AISI 52100
†AISI C-3135 steel pin vs AISI-C-1137 v-blocks
‡With 1% thiadiazole type of additives. The Shell Four-Ball weld point of the resultant grease was 620 kg

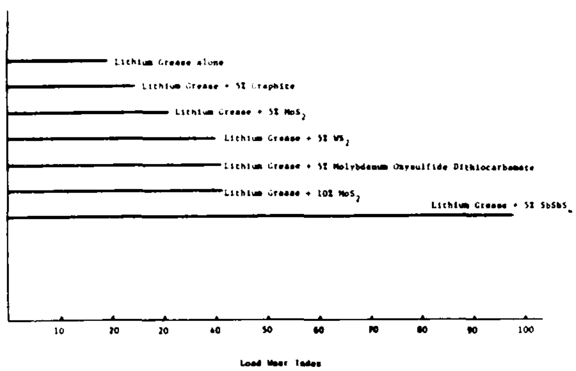

Fig.3—Load wear indexes of various solid additives in lithium grease (AISI-C-52100 steel balls).

TABLE 6—FALEX LOAD-CARRYING PROPERTIES* OF GREASES

GREASE + ADDITIVE	FAILURE LOAD (lbs)
Lithium Grease	< 300
Lithium Grease + 5% MoS_2	1850
Lithium Grease + 5% $SbSbS_4$	2250
Silicone Grease	< 300
Silicone Grease + 5% MoS_2	< 300
Silicone Grease + 5% $SbSbS_4$	< 300
Clay Grease	2850
Clay Grease + 5% MoS_2	2850
Clay Grease + 5% $SbSbS_4$	3200
Aluminum Complex Grease	1000
Aluminum Complex Grease + 5% MoS_2	1700
Aluminum Complex Grease + 5% $SbSbS_4$	2100

*ASTM D 3233

TABLE 7—LUBRICATING PROPERTIES OF VARIOUS GREASES CONTAINING $SbSbS_4$ AND MoS_2 WITH STAINLESS-STEEL BALLS (AISI-440C)

GREASE COMPOSITION	SHELL FOUR-BALL WELD POINT (kg)	LOAD WEAR INDEX
Lithium Grease	80	3.50
Lithium Grease + 5% $SbSbS_4$	450	48.4
Lithium Grease + 5% MoS_2	100	6.14
Silicone Grease	80	2.9
Silicone Grease + 5% $SbSbS_4$	400	28.8
Silicone Grease + 5% MoS_2	80	3.28
Clay Grease	100	5.04
Clay Grease + 5% $SbSbS_4$	250	19.2
Clay Grease + 5% MoS_2	80	7.01
Aluminum Complex Grease	100	2.43
Aluminum Complex Grease + 5% $SbSbS_4$	250	18.3
Aluminum Complex Grease + 5% MoS_2	100	3.98

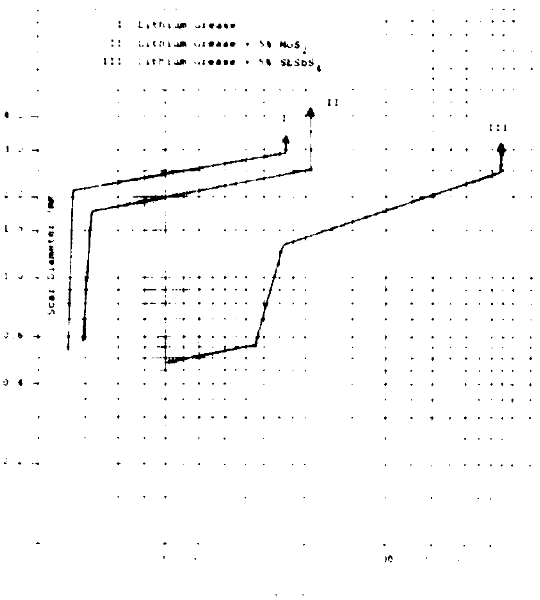

Fig. 4—Scar diameter vs load; AISI-440-C stainless-steel balls, 25°C, 1800 rpm, 10 s.

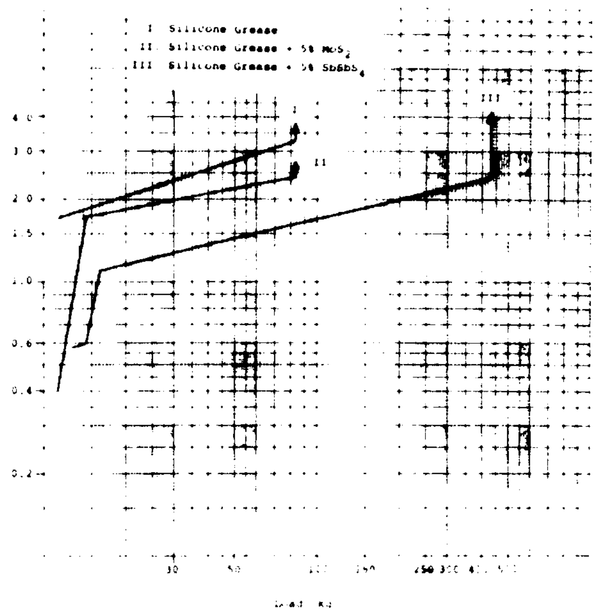

Fig. 5—Scar diameter vs load; AISI-440-C stainless-steel balls, 25°C, 1800 rpm, 10 s.

TABLE 8—COMPARISON OF SHELL FOUR BALL WEAR RESULTS OF $SbSbS_4$ AND MoS_2 ON CHROME STEEL AND STAINLESS-STEEL BALLS

GREASE AND ADDITIVE	TEST BALL COMPOSITION	WEAR SCAR DIAMETER IN MILLIMETERS (10 s, 1800 rpm RUNS AT THE FOLLOWING APPLIED LOADS IN KILOGRAMS)														
		40	50	60	80	100	126	160	200	250	400	450	500	560	710	760
Lithium Grease + 5% MoS_2	52100*	0.56	0.56		1.43				2.55	weld						
	440†	2.00	2.13		2.38	weld										
Lithium Grease + 5% $SbSbS_4$	52100		0.50						1.00		1.48		1.74		2.18	weld
	440	0.50	0.52	0.55	1.26				1.88		2.40	weld				
Clay Grease + 5% MoS_2	52100	0.36		0.77	0.68	0.85		2.04		weld						
	440	1.84		1.87	2.10	2.28	weld									
Clay Grease + 5% $SbSbS_4$	52100	0.47			0.71	0.72			1.23		1.46			weld		
	440	1.53		1.60	1.71	1.73		2.28	2.89	weld						
Silicone Grease + 5% MoS_2	52100	0.88		0.96	0.90	0.97		1.44	weld							
	440	2.29		2.51	weld											
Silicone Grease + 5% $SbSbS_4$	52100	0.64	0.73			0.73			1.16	1.32	1.66		1.96	weld		
	440	1.18		1.51		1.63			2.06	2.22	weld					
Aluminum Complex Grease + 5% MoS_2	52100		0.50		0.57	1.93		2.24	weld							
	440	2.48	2.62	3.28	weld											
Aluminum Complex Grease + 5% $SbSbS_4$	52100		0.37		0.51			0.89	1.20		2.02	weld				
	440	1.27		1.36	1.60	1.68			2.60	weld						

*Chrome steel AISI-C 52100
†Stainless steel AISI 440C

ditive for use under extremely high loads where the conventional solid lubricants are found to be inadequate.

ACKNOWLEDGMENTS

This work has been supported by the Office of Naval Research. The authors are grateful for the guidance and advises provided by Hal Martin of the Office of Naval Research on various aspects of this program. They also acknowledge the generous assistance of Paul Tubbs of Keystone Lubricant Division, Pennwalt Corporation

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DISCUSSION

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The authors should be commended for doing an excellent piece of work in the field of complex metal chalcogenides. This is to be expected since they have been doing extensive work in this field for many years. It is particularly interesting to note the results with stainless steel and silicone greases since each, in it's own way, has inherent lubricating problems.

Have the authors run or are they contemplating running any tests with antimony thioantimonate to ascertain it's value in resin-bonded solid film lubricants?

DISCUSSION

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The potential of complex chalcogenides such as $SbSbS_4$ as improved solid lubricant materials especially for hard-to-lubricate metals has been well documented [authors' references and (*B1*)] and this paper with its wealth of data continues to demonstrate this potential.

A property common to complex chalcogenides is that they are amorphous solids. This property is in contradiction to what has been generally considered to be a necessary but not sufficient requirement of a good solid lubricant, namely a layer-lattice structure. Would the authors care to comment on this observation? Is there any evidence that the thioantimonate anion is really present, that is, Sb in the +5 oxidation state and the Sb cation in the +3 oxidation state, or is it possible that a co-precipitation took place in which sulfur was intercalated into the structure of Sb_2Sb_3?

In the preparation of complex chalcogenides such as $FeMoS_4$, the resultant product is really a mixture of FeS_2 and MoS_2 but in an intimately mixed state due to co-precipitation. Physically mixing FeS_2 and MoS_2, however, would not provide the same beneficial results. Finally, how reproducible are these results from batch-to-batch preparations and what is the anticipated cost of $SbSbS_4$ relative to MoS_2?

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DISCUSSION

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The authors have presented some very interesting results concerning a new lubricant additive, "antimony sulfide." Their basic conclusion is that it is much better than MoS_2 in that it increases the weld load to extremely high values even with difficult-to-lubricate metals such as stainless steel.

Since the authors have used standard test devices, the results more or less speak for themselves. There are, however, a few general questions which can be raised.

1. MoS_2 does not yield a particularly high weld load when used in greases. Have the authors compared their results with organic sulfides such as di-benzyl, di-phenyl, or di-octyl?
2. Do the authors intend a direct comparison with MoS_2? In other words, are they proposing that they are more or less interchangeable for the same types of application? If so, do they have a comparison of the two compounds dry?
3. Would the authors speculate on the mechanism of lubrication with this compound? Is it a low shear strength material, or is there some sulfur reaction which gives the high weld loads?

AUTHORS' CLOSURE

In reply to a point raised by both Messrs. Conte and Peterson concerning the possible lubrication mechanism of antimony thioantimonate—the fact that this amorphous sulfide is so effective as a lubricant is intriguing to us. Work is in progress both at the National Bureau of Standards and at our company to investigate different aspects that may shed light on the mechanism.

In response to the questions raised by Mr. Peterson regarding comparison of results of organic disulfides and MoS_2 with antimony thioantimonate—the reason that we listed the performance data of MoS_2 is solely for reference. The weld points of the same base grease containing an organic disulfide have been determined and the results are given in Table D1. A study using antimony thioantimonate as a dry lubricant has been undertaken by the National Bureau of Standards.

Mr. Conte raised an interesting question regarding a possible structure of antimony thioantimonate which may result from elemental sulfur intercalated into Sb_2S_3 lattice. Intercalation consists of insertion of a guest species into a host structure with substantial retention of the structural features of the host. Virtually all of the intercalation compounds exhibit X-ray diffraction patterns which are differ-

TABLE D1—WELD POINTS OF LITHIUM GREASE CONTAINING VARIOUS ADDITIVES

	WELD POINT, kg
Lithium Grease	140
Lithium Grease + 5% MoS_2	250
Lithium Grease + 5% Dibenzyl Disulfide	180
Lithium Grease + 5% Diphenyl Disulfide	160
Lithium Grease + 5% Dioctyl Disulfide	126*
Lithium Grease + 1% $SbSbS_4$	400
Lithium Grease + 5% $SbSbS_4$	760

*Dioctyl disulfide is a liquid at room temperature and the grease structure was destroyed upon addition of 5% dioctyl disulfide. This may explain that its weld point is lower than the base grease.

ent from those of the hosts because of expansion of lattices. Since antimony thioantimonate is amorphous, formation of an intercalation structure in this case is doubtful.

Good reproducibility on elemental analysis and performance results has been obtained from different batches of antimony thioantimonate. An estimate cost of antimony thioantimonate will be available upon completion of our current scale-up study.

APPENDIX II

EFFECT OF ANTIMONY THIOANTIMONATE IN GREASES ON ABRASIVE WEAR

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Abstract: There is a crucial need for effective lubricant additives that are capable of preventing damage that may occur due to contamination of lubricating systems by abrasive particles. This is an essential requirement for lubricants used in equipment and military vehicles that are operated in sandy environments. The effect of antimony thioantimonate ($SbSbS_4$) in three base greases—MIL-G-10924, MIL-G-24139, and MIL-G-81322—was investigated. The presence of $SbSbS_4$ in these greases provided considerable improvements in weld point, load wear index, and wear prevention properties with two different alloys. Moreover, impressive wear resistance properties were imparted by low concentrations of $SbSbS_4$ in these greases deliberately contaminated with hard abrasive particles. The combination of outstanding EP and antiwear characteristics and anti-abrasion properties of antimony thioantimonate makes this material an attractive candidate as a grease additive. Extensive field testing of greases containing this material is recommended.

Key words: Solid lubricant additive; antimony thioantimonate; abrasive wear; extreme pressure and antiwear properties; greases.

INTRODUCTION

Abrasive wear is well recognized as the primary cause of surface damage for military vehicles and equipment as well as industrial machinery.[1] This form of wear is encountered when foreign materials, e.g., sand, grit or other hard

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particles become entrained in the lubricant. Sources of such hard particles include airborne contaminants entering the system during equipment assembly or repair, finely divided wear products from system components, fine debris resulting from oxidation or corrosion, and operation in sandy environments. Accordingly, a critical property of a lubricant material or additive is its ability to prevent or minimize component wear in the presence of hard abrasive particles.

Antimony thioantimonate ($SbSbS_4$), when incorporated into a number of selected greases as a solid additive at low concentration, imparts outstanding extreme pressure properties on both chrome tool and stainless steels.[2] An initial evaluation of $SbSbS_4$ in several military greases was conducted with the objective of selecting one or more of these greases to be formulated with $SbSbS_4$ for field evaluation involving sandy environment. To investigate additive response in the presence of abrasives, a grit material having precise composition and known particle size was incorporated into those greases with and without the presence of $SbSbS_4$. The extreme pressure and antiwear characteristics of these greases with and without $SbSbS_4$ and MoS_2 as additives were determined and compared.

PREPARATION OF ANTIMONY THIOANTIMONATE ($SbSbS_4$)

Antimony thioantimonate was prepared by the modified procedures as described in Progress Report No. 7. A large supply of this material was synthesized in preparation for the coming field evaluation.

GREASES

Three fully formulated greases meeting the following military specifications were used as base materials:

- MIL-G-10924 - Grease, Automotive and Artillery (GAA)
- MIL-G-24139 - Grease, Multipurpose Quiet Service
- MIL-G-81322 - Grease, Aircraft General Purpose Wide Temperature Range

GRIT MATERIAL

The grit material used in abrasive study was supplied by the A/C Division of General Motors Corporation, Flint, Michigan. It has an average particle size of 60-80 μ and the following composition:

SiO_2	68%
Fe_2O_3	5%
Al_2O_3	16%
CaO	3%
MgO	1%
Na_2O	5%
Ignition Loss	2-3%

TEST METHODS

Falex Machine

The abrasive wear study was carried out on a Falex machine using AISI-C-3135 steel pins (R_b87-91) and AISI-C-1137 V-blocks (R_c20-24). The testing speed, temperature, and load were 290 rpm, 77°F, and 100 lbs, respectively. The following procedures were employed.

1. Test specimens (pin and V-blocks) were cleaned with xylene followed by acetone and then air dried.

2. Test pin was inserted in pinholder.

3. Grooves of V-blocks were filled with grease sample and struck flush.

4. V-blocks were set in their sockets.

5. Jaw loading assembly was mounted on lever arms.

6. Jaw load was brought to a gauge load of 100 lbs (manual turning of ratchet wheel).

7. Drive motor was started and test run to 30 seconds, or to failure if prior to 30 seconds. Failure was indicated by rupture of pin or rapid torque increases above 40 in-lb and excessive noise.

8. Test pin was cleaned with xylene and acetone before making visual observation.

Four-Ball Testers

The extreme pressure and antiwear properties of the greases were determined on Shell Four-Ball EP and Wear Testers. These testers consist of steel spherical specimens sliding against each other. Weld points and load wear indices were determined in a series of runs (10 sec., 1800 rpm at 77°F) conducted at various loads, and scar diameters were measured after each run in accordance with ASTM-D-2596. Wear

prevention characteristics were determined by measuring scar diameters of test specimens after each run at specified rpm, load, temperature and duration (ASTM-D-2266). Two alloys—chrome tool steel AISI-C-52100 and stainless steel AISI-440C—were used.

RESULTS AND DISCUSSION

Abrasive Wear Study

Abrasive wear tests were conducted with the Falex machine for the three base greases (MIL-G-10924, MIL-G-24139, and MIL-G-81392), the three base greases with 5% MoS_2, the three base greases with 5% $SbSbS_4$, and same modified greases containing abrasive particles. The results for the abrasive wear resistance imparted by 5% concentration of $SbSbS_4$ in MIL-G-10924 and MIL-G-24139 greases are presented in Figure 1. It can be observed that severe wear and surface damage occur with either MIL-G-10924 or MIL-G-24139 (both containing 5% grit); however, $SbSbS_4$ virtually eliminates such wear and surface damage. Wear effects were also noted with MIL-G-81322 in the presence of abrasive particles, although the base grease is originally formulated to provide some degree of protection from surface damage in sliding contact. The presence of $SbSbS_4$ further improved the antiwear properties of this grease. The presence of MoS_2 in all the three base greases also provides some degree of surface protection; however, by visual observation the results are not as evident in all cases as those obtained with $SbSbS_4$.

Extreme Pressure and Antiwear Properties

As indicated earlier, all three base greases studied had been fully formulated at the source in order to meet the military specifications, i.e., they contained additives. Our primary interest was to improve abrasive wear resistance of these greases by incorporation of $SbSbS_4$; however, the extreme pressure and antiwear properties were also obtained in order to determine whether these performance properties were further improved by the presence of $SbSbS_4$.

We found that the weld points and load wear indices of MIL-G-10924 could be considerably improved by the presence of 1 to 5% $SbSbS_4$. At 5% concentration of MoS_2 no increase in weld point of this grease was observed; however, its load wear index was somewhat higher than the base grease. Indeed, the EP properties of the base grease containing 1% $SbSbS_4$ were found to be superior to those of the same base grease containing 5% MoS_2. The antiwear characteristics of

the base grease containing 1% $SbSbS_4$ showed slight improvement over its base grease. The experimental data are recorded in Table I. A graphical comparison of the data obtained on these greases is presented in Figure 2.

The weld point and load wear index of MIL-G-24139 containing 1% $SbSbS_4$ were significantly higher than those of the base grease. The weld point and load wear index of the base grease containing 5% MoS_2 were lower than that of the same base grease containing 1% $SbSbS_4$. The wear prevention characteristics of samples of the base grease containing 1% $SbSbS_4$ and 5% MoS_2, respectively, were comparable and were a dramatic improvement over the base grease on both chrome tool and stainless steels. The experimental data are recorded in Table II and a graphical presentation is shown in Figure 3.

Because of insufficient supply of MIL-G-81322 grease available to us at this time, load wear indices were not determined. The weld points of MIL-G-81322 containing 1 and 3% $SbSbS_4$ showed 25 and 100% improvements over the base grease, respectively. With 5% MoS_2 a weld point increase of 56% was observed. The base grease, as originally formulated, showed good wear prevention characteristics on chrome tool steel. No significant improvement of wear prevention characteristics on both chrome tool and stainless steels was achieved by incorporation of MoS_2 or $SbSbS_4$ into the base grease. The results are listed in Table III.

CONCLUSIONS

1. The abrasive wear resistance of both MIL-G-10924 and MIL-G-24139 greases was dramatically improved by incorporation of low concentrations of $SbSbS_4$.

2. The extreme pressure and antiwear properties of three base greases—MIL-G-10924, MIL-G-24139, and MIL-G-81322—were greatly enhanced by using $SbSbS_4$ as a solid additive. At a lower concentration this additive outperformed MoS_2 in all cases.

3. Antimony thioantimonate showed good response to both chrome tool steel AISI-C-52100 and stainless steel AISI-440C in all three base greases investigated.

4. If the presence of $SbSbS_4$ in these three base greases does not adversely affect other properties such as water washing out, rust prevention, drop point, etc. (investigation of some of these properties is planned), the use of $SbSbS_4$ as a solid additive in these greases

[illegible] be [illegible]ly beneficial.

5. These results with $SbSbS_4$ as extreme pressure and anti-wear agent indicate potential for significant impact covering major improvements for lubricating greases, especially the current MIL-G-10924 (GAA) improvements being pursued by the U. S. Army Mobility Equipment Research and Development Command (DRDME-GL), Fort Belvoir, Va.

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Table I. Weld Points, Load Wear Indices, and Wear Scar Diameters of MIL-G-10924 Grease Containing Additives

Grease Composition	Weld Point,[1] kg	LWI[1]	Wear Scar[2] Diameter, mm
MIL-G-10924 Grease (GAA)	160	29.3	0.62
" + 1% $SbSbS_4$	250	39.4	0.59
" + 5% $SbSbS_4$	315	56.7	0.59
" + 5% MoS_2	160	38.4	0.57

1. ASTM-D-2596 - AISI 52100 Steel
2. ASTM-D-2266 - 1200 rpm, 40 kg, 167°F for one hour on AISI 52100 steel

Table II. Weld Points, Load Wear Indices and Wear Scar Diameters of MIL-G-24139 Grease Containing Additives

Grease Composition	Chrome Tool Steel 52100			Stainless Steel 440-C
	Weld Point[1] kg	LWI[1]	Wear Scar Diameter[2] mm	Wear Scar Diameter[3] mm
MIL-G-24139 Grease (AMI)	126	14.1	2.17	3.48
" + 1% $SbSbS_4$ [4]	315	38.1	0.58	2.18
" + 2% $SbSbS_4$	---	----	0.56	----
" + 1% MoS_2	---	----	0.64	2.55
" + 5% MoS_2	200	27.9	0.57	2.15

1. ASTM-D-2596
2. 40 kg, 77°F and 1800 rpm for 5 min.
3. 20 kg, 77°F and 1800 rpm for 5 min.
4. The presence of $SbSbS_4$ in MIL-G-24139 did not cause copper corrosion according to ASTM-D-130 (212°F for 1 h).

Table III. Weld Points and Wear Scar Diameter of MIL-G-81322 Grease Containing Additives

Grease Composition	Chrome Tool Steel 52100		Stainless Steel 440-C
	Weld Point[1] kg	Wear Scar Diameter[2] mm	Wear Scar Diameter[4] mm
MIL-G-81322 Grease (MOB)	160	0.41	2.31
" + 1% $SbSbS_4$	200	0.39	2.19
" + 3% $SbSbS_4$	315	0.56	1.88
" + 5% MoS_2	250	0.41	1.90

1. ASTM-D-2596
2. 40 kg, 77°F, and 1800 rpm for 5 min.
3. 20 kg, 77°F, and 1800 rpm for 5 min.

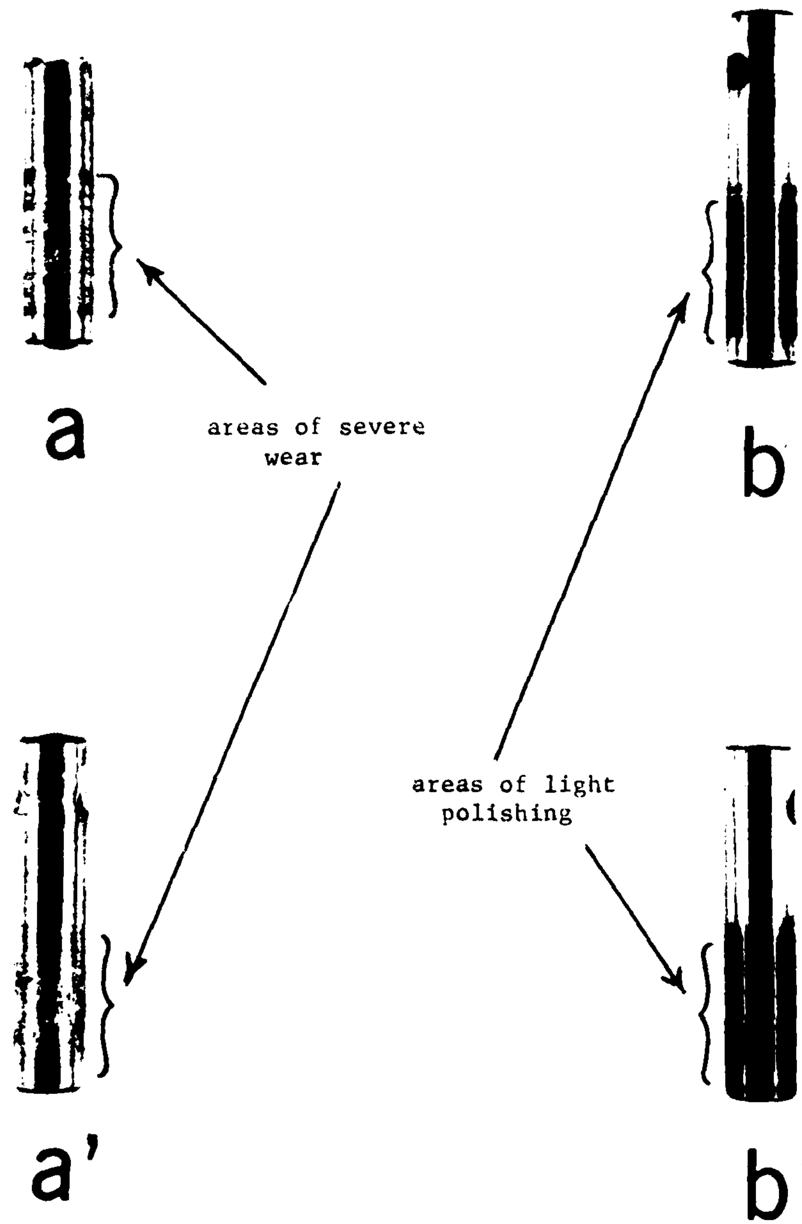

Figure 1. Effect of $SbSbS_4$ on Abrasive Wear

The outstanding wear resistance properties imparted by $SbSbS_4$ to greases containing grit particles (primarily SiO_2 60-80 μ) are illustrated by these Falex pins

a = grease MIL-G-24139 with 5% grit
b = " " " " and 5% $SbSbS_4$
a' = " MIL-G-10924 " "
b' = " " " " and 5% $SbSbS_4$

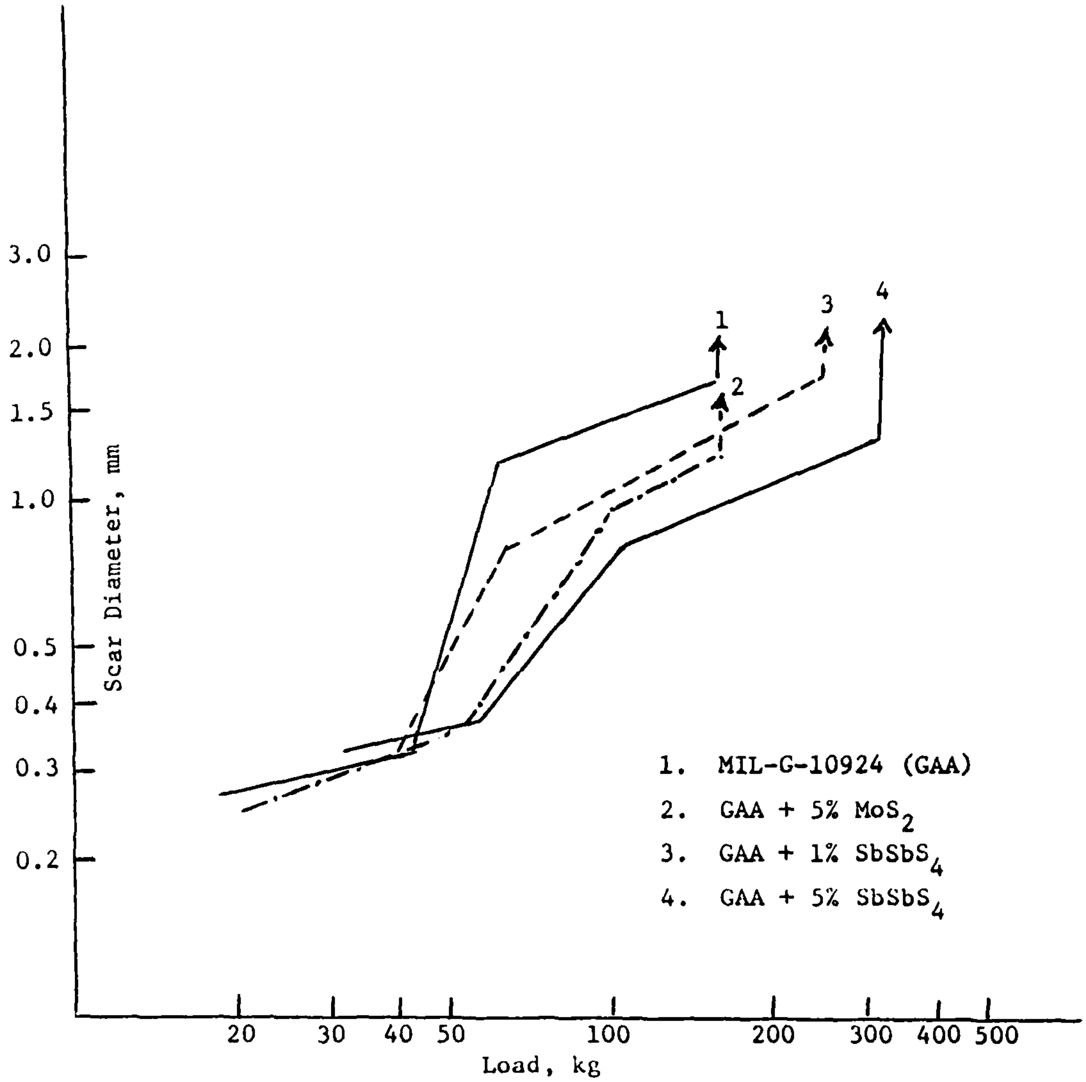

Figure 2. Wear Scar Diameter vs. Load; AISI-C-52100 Steel Balls; 25°C, 1800 rpm, 10s

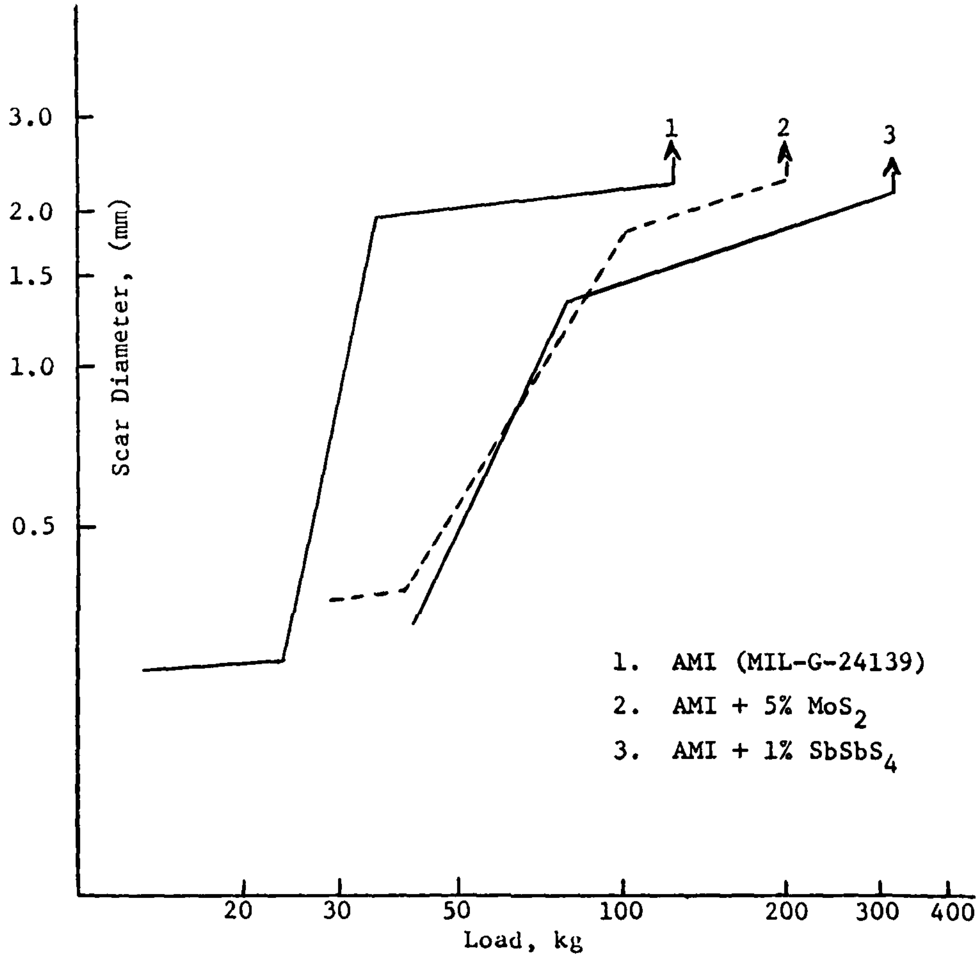

Figure 3. Wear Scar Diameter vs. Load; AISI-C-52100 Steel Balls; 25°C, 1800 rpm, 10s

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